

DRAFT  
PYRETHROID LABORATORY WORKSHOP  
MEETING NOTES  
31 AUGUST 2005

**Participants:** Jim Atherstone (S SJ ID), Denis Barry (FGL Environmental), Ron Boquist (The Twining Laboratories, Inc.), Dawn Carlton (S SJ WQC), Jim Carter (EMAX Laboratories, Inc.), Dave Crane (CDFG-Water pollution Control Lab), Bill Croyle (CVRWQCB), John Eisner (California Laboratory Services), David Elliott (Environmental MicroAnalysis, Inc.), Stephanie Fong (CVRWQCB), Sheri Fox (National Resource Conservation Service), Scott Furnas (California Laboratory Services), Rich Gossett (CRG Marine Labs), Peter Halpin (Caltest Analytical Laboratory), Cynthia Heed (APPL Labs, Fresno), Rick Heines (Caltest Analytical Laboratory), Michelle Hladik (USGS), Dania Huggins (CVRWQCB), Humberto Izquierdo (Napa County), Mike Johnson (UC Davis), Julie Anne Langill (CVRWQCB), Devra Lewis (CVRWQCB), Karl Longley (CVRWQCB Board), Abdou Mekebri (CDFG-Water pollution Control Lab), Jim Markle (CURES), Melissa Morris (CVRWQCB), Michael Niemi (Modesto ID), Sandy Nurse (Sierra Foothill Lab), Todd Poyfair (Columbia Analytical Services), Margie Lopez read (CVRWQCB), Lilia Rivera (CDFA), Mat Rogers (UC Berkeley, UOP, LBNL), Jay Rowan (CVRWQCB), Claus Suverkropp (Larry Walker Associates), Amanda Smith (CVRWQCB), Keith Starner (DPR), William Stringfellow (University of Pacific), John Swanson (CVRWQCB), Joseph Ureno (The Twining Laboratories, Inc.), Leticia Valadez (CVRWQCB), Dan Walige (OSPR), Don Weston (UC Berkeley), Elaine Wong (CDFA), and Michelle Wood (URS Corp.)

## **INTRODUCTIONS**

Dr. Karl Longley, Regional Board member, and Margie Lopez-Read, Chief, Monitoring and Assessment Unit, Irrigated Lands Program, welcomed everyone and gave a brief introduction of the purpose of the workshop and their roles. General introductions of attendees were conducted.

## **I. IRRIGATED LANDS PROGRAM BACKGROUND**

### **A. Monitoring Objectives**

Margie Lopez-Read gave an overview of the workshop objectives, which included the Irrigated Lands Conditional Waiver Program needs for pyrethroid analyses in sediment and the current analytical capabilities, time for a group discussion and potential for a laboratory round table.

### **B. Irrigated Lands Program**

A background of the Irrigated Lands Program was given, and the discussion in the Program's Technical Issues Committee (TIC) and particularly the Sediment Toxicity Focus Group were also introduced. Main points included the Monitoring and Reporting Program (MRP) requirements, the recommendation for pyrethroid analyses in sediment and the currently insufficient laboratory services available for coalitions.

### **C. Pending Monitoring Requirements**

The possibility of a laboratory round table to discuss not only Pyrethroid issues but also any laboratory related issues that arise within the Irrigated Lands Program was also presented.

## **II. ANALYTICAL APPROACHES**

### **A. Current Limitations in Pyrethroid Analyses**

Dr. Don Weston of UC Berkeley presented next on his perspective on the analytical needs for interpretation of sediment toxicity. Dr. Weston first gave a brief description of the Hyalella toxicity test as well as the frequency of Hyalella sediment toxicity in the Central Valley based on results from his UC Berkeley lab as well as from Pacific EcoRisk. Next, the topic of identifying the contributors to sediment toxicity, namely by examination of the Toxicity Unit (TU) was presented. The correlation of Pyrethroid TU's to Hyalella toxicity was presented. Finally, Dr. Weston presented a summary table of reporting limits for Pyrethroid analyses in order to assess sediment toxicity.

### **B. Existing methods**

John Swanson of the Irrigated Lands Program next introduced a table (Table 1) outlining the currently available methods for analysis of pyrethroids in sediment. A discussion period was held with the following points being discussed:

CDFG: Abdou Mekebri's comments:

- They have been working for years with the Gas Chromatography with an Electron Capture Detector (GC ECD) method for the analysis of pyrethroids in sediments (extreme sensitivity of the detector). Currently, they are working with USGS to lower their reporting limit by this method in order to meet Don Weston's requested 1ug/kg dry weight reporting limit.
- They have run trials with High Resolution Mass Spectrometry
- GPC method. Some of the Pyrethroids have multiple isomers, but these are not identified in extraction. During the extraction (prior to instrument analysis) process they can only identify some of the isomers (1, 2, or 3), while with ECD you can obtain all the isomers. There are no standards to measure these compounds.
- GC ECD method. During the extraction process there are three "clean ups:" Florisil, GPC, and one other.
- GC ECD method. The recovery is about 70-100% with an average of 100%.
- They have also been looking at deltamethrin analyses. However, the source of this pyrethroid is not generally relevant to agricultural run off.

Note: Extraction is only the process of transferring the analyte of interest from the matrix submitted (sediment or water) into the matrix that is suitable for the instrument (solvent).

USGS: Michelle Hladik

If the source of the sample is from urban run off or storm water, the pyrethroids found in these samples may be non-halogenated (Resmethrin, sumethrin, allethrin, and the Pyrethrins) so they will not work with the GC ECD method. USGS is developing GC-MS methods for pyrethroid analysis.

#### Caltest Analytical Laboratory: Peter Halpin

- It is also important to consider the biological breakdown time of the compounds. DPR was investigating using methanol as a chemical preservative. This is only applicable to water samples. The short hold times are related to waters (i.e. cyhalothrin three days of holding time, page 9 of NorCal SETAC News- Summer 2005). In the case of sediments, if sediments are stable for months after being frozen. If sediments are immediately frozen, hold times are not expected to be an issue, as previously mentioned by Don Weston.
- Reference material to evaluate individual samples of sediment is about \$1,000. Environmental Resources Associates (ERA) offered to provide performance evaluation samples for \$1,000/ea as a one off kind of preparation. The approximate cost for ERA to produce six PT samples four times a year will be \$3700.00 plus \$10.00 per shipping location plus shipping charges. This works out to \$154 per QC sample (called performance test (PT) sample or performance evaluation (PE) sample). In summary, to include a third party verification of method performance is a very reasonable cost per sample when a set of performance samples was ordered as part of a program.
- The GC/MS selected ion monitoring method we referenced (and was included in the handout of the NorCal SETAC publication) is wholly based on EPA method 8270, with the modification of running the mass spectrometer in a narrow range scan for the three most abundant ions. This modification of using a narrow range selected ion scan instead of the traditional full scan approach yields the necessary sensitivity to analyze the pyrethroids at environmentally relevant levels of low ng/l. Otherwise, the method is an 8270 procedure using a pyrethroid analyte list. As noted earlier, the GC/MS method is capable of monitoring all the pyrethroids including those that are non-halogenated which are not detectable by the GC/ECD method.

#### CVRWQCB.

- These methods need to be implemented by December 2005.
- The demand of analysis just for the Irrigated Lands Program is about 500 samples per year. Region 4 will also require some analyses, TMDL exploration of replacement chemicals for organophosphates, and storm water programs may also be expanding to pyrethroid analyses.
- The Central Valley Regional Board would also like to start up a Laboratory Roundtable in order to have an approach to coordinate work that laboratories conduct for the Irrigated lands Program. Broad interest in participation among workshop attendees was expressed in this idea.

#### Summary

The Laboratory Workshop was a success in terms of getting to know where the current status of laboratory capability with respect to analysis of pyrethroids in sediment. Also, the meeting provided an opportunity for Irrigated Lands Program staff to define pending

program needs and establish a mechanism to work with laboratories in achieving lower detection levels.

There was broad interest in the possibility of developing lower detection limits with laboratories as well as exploring the potential for round robin testing.

#### Other points mentioned

- Continue to explore advances in pyrethroid analyses in sediment (mention was made of studies in Australia)
- Define the detection levels that will be most effective to explain toxicity and share with workshop attendees.
- Pursue the possibility of developing a Round Robin for pyrethroids in sediment for interested laboratories
- Initiate a Laboratory Roundtable for laboratories that are conducting work for coalitions and individual dischargers with the Irrigated Lands Conditional Waiver Program.